

An MDL is not a static value. Yesterday I ran an annual MDL determination and it jumped to 0.21 mg/l from last year's 0.10 mg/l. Some of my methods MDLs do appear to vary very little from year to year but that might not be the case for other labs.

I have other concerns. MDL are calculated values that may not reflect actual results, especially if instrument response is non linear below a certain value. As an example, Ammonia ISE probes will not read linearly at low concentrations under normal conditions. So an MDL for this method is irrelevant at best. A demonstration of linearity might be more appropriate for some methods, with a cutoff at a limit such as 25% error from the true value.

Other factors also affect low level readings, a common one being the calibration curve. The y-intercept often will not go through zero (in our lab we use linear calibrations and are not allowed to force it through zero). It is quite possible to run a perfect no-signal blank and get either a negative number or a result above the MDL due entirely to the calibration. Both scenarios are unacceptable and limits on the y-intercept to produce a result of  $\pm 1/2\text{MDL}$  or better with no signal would be advisable. Without this limitation, the MDL and the PQL become meaningless and subject to manipulation. If we had the flexibility to force the calibration curve through zero and if the instrument read nothing but positive values this would not be a problem. EPA needs to address these problems and allow forcing calibrations through zero in some cases.

Some laboratories may take the published rules and extend them way beyond what the EPA originally intended. At our lab there has been some discussion of analyst MDLs because different analysts obtain different MDLs when performing their proficiency testing. The end result would be that each analyst would report their own unique MDL for the analyses they carried out. I do not agree with this because as I understand the EPA procedure, the preference is to obtain the MDL from separate analyses done over a period of time. I believe it should also include results from different analysts too, if available. Initial or individual MDL determinations that are done all from the same analysis run on the same day tend to yield lower values. Those results gathered over a period of weeks or months can give more realistic MDL values. EPA needs to clarify this.

The current EPA MDL procedure advises to do a blank correction only if it is usually done for regular samples. The procedure is to subtract the average of all the blanks from each result. I see many problems with this, the first one being that many analysts do the blank subtraction even when not done for the regular samples. Then, some do not include negative blank values and this biases the result. For some analyses, blanks are subtracted only if they exceed a certain value, so subtracting the average blank result may also bias the MDL. Another problem with subtracting the blanks when not done for regular samples is that the reported average recovery is lowered. EPA has not addressed average recovery in the current MDL procedure. This would give rise to a situation like this: A spike of 0.50 ppm after blank correction of 0.20 results in 0.30 ppm and an MDL of 0.06 ppm. So we have excellent precision but, on paper at least, lousy accuracy. Note also in that example how the blank can often be higher than the MDL. I believe that changing the spike-to-MDL ratio from 10 to 5 as is being proposed will only make this worse. In the above example, a spike of 0.30 ppm would be required, which after blank correction would result in 0.10 ppm. EPA needs to include a spike percent recovery limit that should trump the MDL-to-spike ratio when exceeded.

In fact, whether the blank is subtracted or not, the MDL will not change because it is based on the variance from the average. Some methods could have either a high or low blank level and it won't make any difference on the MDL determination. Not only that, but the calculated MDL can be lower than the actual blank levels. EPA should make the blank result a part of the procedure in such a way that the MDL is always larger, perhaps by adding the average blanks to the calculated MDL.

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